

# UK Patent Application GB 2 258 258 A

(43) Date of A publication 03.02.1993

(21) Application No 9215569.6	(51) INT CL <sup>6</sup> C09K 7/06
(22) Date of filing 22.07.1992	(52) UK CL (Edition L) E1F FGP
(30) Priority data (31) 9116277 (32) 27.07.1991 (33) GB	(56) Documents cited None
(71) Applicant David Brankling 5 Spring Tyne, Westhill, Skene, Aberdeenshire, AB32 6NH, United Kingdom	(58) Field of search UK CL (Edition K) E1F FGP INT CL <sup>6</sup> C09K On-line data base: WPI
(72) Inventor David Brankling	
(74) Agent and/or Address for Service Murgitroyd & Company 373 Scotland Street, Glasgow, G5 8QA, United Kingdom	

## (54) Drilling fluid emulsion composition

(57) A drilling fluid composition in which the continuous phase of an emulsion comprises a linear alkyl benzene. Preferably the alkyl group has from 4 to 40 carbon atoms.

GB 2 258 258 A

1     "Drilling Fluid"

2

3     This invention relates to drilling fluid for use in the  
4     drilling of wells.

5

6     Drilling fluids are circulated down a wellbore during  
7     well drilling operations. The fluid is usually pumped  
8     down a central drillstring, passes through the drill  
9     bit into the wellbore and then returns to the surface.  
10    The fluid is then recovered, solid materials extracted,  
11    processed and reused.

12

13    Drilling fluids are required to remove rock cuttings  
14    generated during the boring process, to lubricate and  
15    cool the drill bit and maintain the integrity of the  
16    hole. Physical properties of the drilling fluid such  
17    as viscosity, density, salinity and filtrate loss may  
18    be modified by chemical addition as necessary.

19

20    One major problem which occurs in the use of water  
21    based drilling fluids is the hydration of rock being  
22    drilled; this is particularly acute when the interval  
23    contains clays and shales. These materials exhibit a  
24    great affinity for water and adsorption leads to  
25    swelling of the rock with resultant stresses leading to

1 collapse of the borehole or loss of structure.

2

3 Such failures lead to wellbore expansion, stuck pipe,  
4 excessive rheology, and general drilling problems.

5

6 A second problem with water based drilling fluids which  
7 is particularly prevalent in the North Sea is the  
8 drilling of so called "salt stringers ". These  
9 intervals comprise regions of high concentrations of  
10 water soluble salts such as sodium, magnesium and  
11 potassium chloride which will dissolve in the drilling  
12 fluid and lead to hole enlargement, washout and general  
13 failure of the wellbore.

14

15 One solution to the above problems has been the use of  
16 so called "salt saturated" solutions in which a soluble  
17 salt, usually sodium chloride, is dissolved at maximum  
18 concentration in the aqueous medium and used as the  
19 drilling fluid base. Such solutions limit shale  
20 hydration and prevent further dissolution of drilled  
21 salts into the fluid.

22

23 However, salt saturated solutions are expensive, have  
24 limitations on the density range which may be used and  
25 limit the number of additives which may be used to  
26 control the properties of the drilling fluid.

27

28 A second and more widely applied solution involves the  
29 use of oil based drilling fluids which are usually  
30 formulated with mineral oils. These fluids comprise a  
31 salt-containing aqueous phase which is tightly  
32 emulsified into an external oil phase by the use of  
33 suitable surfactants.

34

35 Oil based drilling fluids therefore present to the

1 surface of drilled rocks an inert oil phase which will  
2 not hydrate shale nor dissolve salt. Further, cuttings  
3 recovered from oil based fluids are covered with a thin  
4 film of oil which prevent hydration and breakage.

5

6 Oil based drilling fluids have a much wider range of  
7 density, rheology, thermal stability and application  
8 than salt saturated or water based fluids and are  
9 widely used.

10

11 However, disposal of rock cuttings which contain a  
12 significant proportion of water insoluble oil,  
13 especially by disposal through marine dumping at the  
14 drill site, is becoming environmentally unacceptable.

15

16 In attempts to upgrade the performance of water based  
17 fluids further additives have been used to attempt to  
18 control shale hydration, for example potassium  
19 chloride, polyacrylamide, polyglycerols, carboxymethyl  
20 derivatives, gilsonite, calcium chloride and sodium  
21 silicate. However, none of these systems have proved  
22 to match the performance of oil based fluids and  
23 importantly have minimal effect in preventing solution  
24 of salt sections.

25

26 There exists a need for an environmentally acceptable  
27 alternative to oil based drilling fluid which exhibits  
28 control of both shale hydration and salt dissolution  
29 and which may be used over the density range covered by  
30 oil based fluids.

31

32 Currently-used oil based drilling fluids are described  
33 as "low toxicity" by virtue of the highly refined  
34 nature of the base oils which contain only a small  
35 percentage of aromatic compounds which can be harmful

1 to marine life or to the product handler. However,  
2 such fluids are very poorly degraded and will remain as  
3 a persistent contaminant at disposal sites for many  
4 years.

5

6 "Low toxicity" oils are produced by a series of  
7 fractionation and occasionally solvent  
8 extraction/precipitation processes from crude oils and  
9 hence contain a broad range of molecular structures  
10 only a small number of which are biodegradable.

11

12 However, hydrocarbons having similar structures to  
13 mineral oil may be prepared synthetically by  
14 polymerisation of ethylene or other unsaturated gases  
15 and liquids in manufacturing processes such as the  
16 Shell higher olefins process (SHOP). The resultant  
17 polyalphaolefins (PAO) are high purity compounds which  
18 because of the linear structure are highly  
19 biodegradable. Such a property would make a highly  
20 desirable alternative fluid to conventional mineral oil  
21 based drilling fluids.

22

23 However, another desirable property of the oil  
24 component of an oil based drilling fluid is that the  
25 oil should have a high flash point to ensure safety in  
26 use and a low freezing point to enable liquid handling  
27 under the low temperatures experienced during winter  
28 use or in low temperature regions of the world.

29

30 The flash point of a polyalphaolefin increases as the  
31 molecular weight increases but unfortunately the  
32 freezing point also rapidly increases such that liquid  
33 handling becomes difficult.

34

35 In addition polyalphaolefins contain a reactive

1 unsaturate terminal grouping which is prone to  
2 oxidation, polymerisation and undesirable reactions  
3 which can lead to a change in the physical properties  
4 of the fluid and could cause problems during the  
5 drilling process.

6

7 Other highly refined mineral oils such as liquid  
8 paraffins or polyalphaolefins stabilised by  
9 hydrogenation to yield liquid paraffins also suffer  
10 from the problem of high freezing point in high flash  
11 point fractions.

12

13 According to the present invention there is provided  
14 drilling fluid comprising an emulsion whose continuous  
15 phase comprises a linear alkyl benzene (LAB).

16

17 The LAB is selected to replace the mineral oil content  
18 of conventional oil based drilling fluids in which the  
19 oil phase may consist of naphthenic, paraffinic and  
20 aromatic oils such as diesel, refined base oils, liquid  
21 paraffins and polyalphaolefins.

22

23 Linear alkyl benzenes provide a high flash point, low  
24 freezing point, stable liquid of good biodegradability  
25 which can be advantageously used to replace mineral oil  
26 in drilling fluid.

27

28 The resultant drilling fluid may be used to replace  
29 conventional "clean oil" drilling muds but is  
30 inherently biodegradable and may be treated or disposed  
31 of safely to the surrounding environment.

32

33 In addition the replacement of paraffinic "clean oil"  
34 by a linear alkyl benzene considerably increases the  
35 polarity of the drilling fluid oil phase such that

1 improved surfactant, emulsion and gellant  
2 characteristics are obtained from mud additives  
3 designed to effect the mud emulsion and convey suitable  
4 rheology to the system.

5

6 The structure of the linear alkyl benzene used as the  
7 hydrocarbon phase of the drilling fluid emulsion is  
8 given by the formula:

9



11

12 where n is an integer from 4 to 40,  
13 preferably 4 to 30 and most preferably 4  
14 to 20.

15

16 The minimisation of branched alkyl benzene content is  
17 necessary to maximise biodegradability of the fluid.

18

19 Suitable compounds may for example be produced by the  
20 reaction of chlorinated paraffins or olefins with  
21 benzene in the presence of Friedel-Crafts catalyst, or  
22 the direct reaction of polyalphaolefin with benzene in  
23 the presence of hydrogen fluoride.

24

25 The resultant LAB may then be used as the external  
26 phase of an oil based emulsion at preferable oil/water  
27 ratios varying from 25/75 to 100/0.

28

29 Additives may be included in the fluid such as fluid  
30 loss additives, weighting agents such as barite and  
31 haematite, and speciality polymers.

32

33 Gelling agents, viscosity-controlling agents and  
34 water-soluble salts may also be present, and  
35 hydrocarbon oil and oil-soluble ester may be included

1 in the continuous phase of the emulsion.

2

3 The emulsified water content of the drilling fluid may  
4 contain dissolved salts such as sodium chloride,  
5 potassium chloride, calcium chloride, potassium acetate  
6 or any other soluble material added to adjust the  
7 resultant salt solution and drilling fluid density or  
8 to change the brine properties to enhance drilling.

9

10 The emulsion may also contain natural brines such as  
11 sea water, aquifer fluids or may be fresh water of  
12 minimal dissolved salt content.

13

14 A component of the drilling fluid composition is  
15 preferably a surfactant which emulsifies the aqueous  
16 phase into the LAB and may typically be an organic  
17 acid, amide, ethoxylate, amine, phosphate, propoxylate  
18 or combination thereof.

19

20 Embodiments of the invention will be described by way  
21 of illustration in the following Examples.

22

23 The flash point of a series of liquid hydrocarbons has  
24 been measured by a closed cup technique in conjunction  
25 with an observed melting point (freezing temperature)  
26 for each material and kinematic viscosity at 40°C.

27

28 Oil type	Flash 29 Point/°C	Freezing Point/°C	Viscosity /cSt
-------------	----------------------	----------------------	-------------------

30

31 Conventional

32 "clean oils"

33 BP 83HF\*

100

-32

2.9

34 Total HDF 200\*

110

-30

3.2

35

1 Alpha olefins  
2 (typical)  
3 C<sub>8</sub> 15 -102 0.7\*\*  
4 C<sub>14</sub> 102 -14 2.75\*\*  
5 C<sub>18</sub> 150 +17 3.3

6

7 Linear alkyl  
8 benzene

9 C<sub>8</sub> - C<sub>10</sub> 123 <-70 3  
10 C<sub>10</sub> - C<sub>12</sub> 130 <-70 4  
11 C<sub>11</sub> - C<sub>13</sub> 135 <-70 4

12

13 \*Trade name

14 \*\*Viscosity at 20°C

15

16 The above figures shown that LAB's exhibit very low  
17 freezing points and high flash points exceeding the  
18 performance of conventional "clean oils".

19

20 However, the precursor polyalphaolefins exhibit much  
21 higher freezing points at equivalent flash points which  
22 may cause problems in liquid handling under typical  
23 field conditions.

24

25 Drilling fluid emulsions in which linear alkyl benzene  
26 is used to replace the oil content of a conventional  
27 clean oil system have been prepared according to the  
28 procedure below.

29

30 An invert emulsion mud was prepared by mixing the  
31 following material quantities together on a Silverson  
32 blender at room temperature:

33

34 187.7 ml of hydrocarbon phase  
35 12 g Kleemul 50 (emulsifier/surfactant

7  
8 Once the drilling fluids had been prepared the mud  
9 rheologies and electrical stability were measured at  
10 49 °C, fluid loss monitored at 121 °C and 500 psi  
11 differential.

12  
13 The prepared fluids were then hot rolled at 121°C for  
14 16 hours and mixed properties remeasured.

15  
16 Linear alkyl benzenes obtained from Shell Chemicals  
17 under the trade names Dobane 83 and Dobane 103 were  
18 compared with a conventional "clean oil" from Shell  
19 branded as Shellsol DMA.

20  
21 The above formulations result in 60/40 oil system of  
22 typical North Sea composition.

23  
24 COMPARATIVE EXAMPLE 1 using Shellsol DMA

26	Apparent viscosity	35 cP
27	Yield point	9.6 Pa (20 lb/100 ft <sup>2</sup> )
28	Plastic viscosity	25 cP
29	Gel strengths	5.3/5.8 Pa (11/12 lb/100 ft <sup>2</sup> )
30	Fluid loss	4.0 ml
31	Electrical stability	279 V

32  
33 After hot rolling sample:

1 Yield point 11.5 Pa (24 lb/100 ft<sup>2</sup>)  
2 Plastic viscosity 24 cP  
3 Gel strengths 4.8/5.8 (10/12 lb/100 ft<sup>2</sup>)  
4 Fluid loss 4.0 ml  
5 Electrical stability 309 V

6

7 EXAMPLE 1

8

9 A drilling fluid was prepared using Dobane 83 a C<sub>8</sub> -  
10 C<sub>13</sub> linear alkyl benzene available from Shell Chemicals  
11 UK Ltd.

12

13 Apparent viscosity 53.5 cP  
14 Yield point 16.8 Pa (35 lb/100 ft<sup>2</sup>)  
15 Plastic viscosity 36 cP  
16 Gel strengths 7.2/6.7 Pa (15/14 lb/100 ft<sup>2</sup>)  
17 Fluid loss 2.0 ml  
18 Electrical stability 166 V

19

20 After hot rolling sample:

21

22 Apparent viscosity 62 cP  
23 Yield point 21.1 Pa (44 lb/100ft<sup>2</sup>)  
24 Plastic viscosity 40 cP  
25 Gel strengths 9.1/10.1 Pa (19/21 lb/100 ft<sup>2</sup>)  
26 Fluid loss 2.2 ml  
27 Electrical stability 495 V

28

29 EXAMPLE 2

30

31 A drilling fluid was prepared using Dobane 103 a C<sub>10</sub> -  
32 C<sub>13</sub> linear alkyl benzene available from Shell Chemicals  
33 UK Ltd.

34

35 Apparent viscosity 62 cP

1 Yield point 21.1 Pa (44 lb/100 ft<sup>2</sup>)  
2 Plastic viscosity 40 cP  
3 Gel strengths 9.1/8.6 Pa (19/18 lb/100 ft<sup>2</sup>)  
4 Fluid loss 2.0 ml  
5 Electrical stability 169 V

6

7 After hot rolling sample:

8

9 Apparent viscosity 75 cP  
10 Yield point 25.9 Pa (54 lb/100 ft<sup>2</sup>)  
11 Plastic viscosity 48 cP  
12 Gel strengths 12.5/13.4 Pa (26/28 lb/100 ft<sup>2</sup>)  
13 Fluid loss 2.4 ml  
14 Electrical stability 612 V

15

16 COMPARATIVE EXAMPLE 2

17

18 A drilling fluid of 50/50 Shellsol DMA (prior  
19 art)/water ratio was prepared by blending the following  
20 materials on a Silverson emulsifier:

21

22 230 ml Shellsol DMA  
23 19.9 g Kleemul 50  
24 8.3 g Lime  
25 4.95 g Emulhivis  
26 232 ml Water  
27 46.35 g Calcium chloride

28

29 The resultant emulsion properties were:

30

31 Apparent viscosity 32.5 cP  
32 Yield point 6.2 Pa (13 lb/100 ft<sup>2</sup>)  
33 Plastic viscosity 26 cP  
34 Gel strengths 3.4/3.4 Pa (7/7 lb/100 ft<sup>2</sup>)  
35 Electrical stability 129 V

1  
2 It is clear that in comparison with Comparative Example  
3 1 the electrical stability value and hence emulsion  
4 stability of the drilling fluid is much reduced.

5

6 EXAMPLE 3

7

8 A drilling fluid according to the formulation given in  
9 Comparative Example 2 was produced using Dobane 83 in  
10 place of Shellsol DMA.

11

12 The resultant emulsion properties were:

13

14 Apparent viscosity (49 °C)	65 cP
15 Yield point	21.1 Pa (44 lb/100 ft <sup>2</sup> )
16 Plastic viscosity	43 cP
17 Gel strengths	8.6/8.6 Pa (18/18 lb/100 ft <sup>2</sup> )
18 Electrical stability	192 V

19

20 A comparison of the properties of this 50/50 emulsion  
21 drilling fluid with the fluid produced in Example 1 at  
22 a 60/40 ratio demonstrates no loss in electrical  
23 stability. That is, the linear alkyl benzene results  
24 in a high stability emulsion although the water content  
25 has increased.

26

27 EXAMPLE 4

28

29 A drilling fluid according to the formulation in  
30 Comparative Example 2 was produced using Dobane 103 in  
31 place of Shellsol DMA.

32

33 The resultant emulsion properties were:

34

35 Apparent viscosity (120 °F) 75.5 cP

1 Yield point 24.5 Pa (51 lb/100 ft<sup>2</sup>)  
2 Plastic viscosity 50 cP  
3 Gel strengths 10.1/11.5 Pa (21/24 lb/100 ft<sup>2</sup>)  
4 Electrical stability 153 V

5  
6 In comparison with Example 2 using a higher 60/40  
7 oil/water ratio the 50/50 emulsion produced shows an  
8 emulsion electrical stability of similar value, that is  
9 of enhanced performance compared to the prior art clean  
10 oil system of Comparative Example 2.

11  
12 Linear alkyl benzene therefore demonstrates improved  
13 stability in high water content drilling fluids and  
14 produces fluids of satisfactory rheology, fluid loss  
15 and thermal stability suitable for drilling operations.

16

17 EXAMPLE 5

18

19 A drilling fluid was prepared using PETRELAB P 400, a  
20 linear alkyl benzene of C<sub>10</sub> - C<sub>12</sub> alkyl side chain  
21 produced by Petroquimica Expanola (PETRESA) of Spain  
22 and commercially available as a detergent alkylate.

23

24 The formulation was compared against the base oil BP  
25 83HF, a conventional clean oil produced by BP  
26 Chemicals.

27

28 Fluids were mixed using a laboratory blender to give a  
29 50/50 system of the following composition:

30

31 109.1 ml P 400 or BP 83HF  
32 12 g Kleemul 50 surfactant emulsifier  
33 6 g lime  
34 2 g Perchem DMB organoclay gellant  
35 from Akzo Chemicals

1           128.2 ml     water  
2           56.2 g       calcium chloride (82-85%)  
3                        barite to give a density of 1.43  
4                       (12 ppg)

5

6   Each fluid was tested for rheology at 49°C and then hot  
7   rolled at 121°C for 16 hours before remeasuring  
8   properties.

9

10	Oil Phase	Akyl benzene P 400 Clean Oil BP 83HF			
11		BHR	AHR	BHR	AHR
12	Apparent viscosity/cP	92	93	65	79
13	Yield point/Pa	12.5	27.8	10.6	17.3
14	Plastic viscosity/cP	79	64	54	61
15	Gels/Pa	4.8/8.2	4.8/9.1	2.9/4.8	3.8/6.2
16	Electrical stability/V	418	580	460	561
17	Fluid loss at:				
18	500 psi/121°C	-	4.4 ml	-	7.6 ml

19

20   The use of an alkylbenzene P 400 gives improved  
21   rheology (increased yield point and gel strengths) and  
22   improved fluid loss control.

23

24

25

26

27

28

29

30

31

32

33

34

35

1    Claims

2

3    1    Drilling fluid comprising an emulsion whose  
4        continuous phase comprises a linear alkyl benzene.

5

6    2    Drilling fluid according to Claim 1, in which the  
7        linear alkyl benzene contains an alkyl group having  
8        from 4 to 40 carbon atoms.

9

10    3    Drilling fluid according to Claim 1, in which the  
11        linear alkyl benzene contains an alkyl group having  
12        from 4 to 30 carbon atoms.

13

14    4    Drilling fluid according to Claim 1, in which the  
15        linear alkyl benzene contains an alkyl group having  
16        from 4 to 20 carbon atoms.

17

18    5    Drilling fluid according to any one of the  
19        preceding Claims, in which the ratio of total  
20        linear alkyl benzene to water in the emulsion is  
21        from 25/75 to 100/0 by volume.

22

23    6    Drilling fluid according to any one of the  
24        preceding Claims, containing also a surface active  
25        agent.

26

27    7    Drilling fluid according to any one of the  
28        preceding Claims, containing also a gelling agent.

29

30    8    Drilling fluid according to Claim 7, in which the  
31        gelling agent is selected from clay, modified  
32        organoclays, polymers and resins.

33

34    9    Drilling fluid according to any one of the  
35        preceding Claims, containing also a weighting

1           agent.

2

3   10 Drilling fluid according to Claim 9 , wherein the  
4       weighting agent is barite.

5

6   11 Drilling fluid according to any one of the  
7       preceding claims, containing also a water-soluble  
8       salt.

9

10   12 Drilling fluid according to any one of the  
11       preceding claims, containing also a material which  
12       controls fluid loss.

13

14   13 Drilling fluid according to any one of the  
15       preceding claims, containing also a  
16       viscosity-controlling agent.

17

18   14 Drilling fluid according to any one of the  
19       preceding claims, containing also a hydrocarbon oil  
20       in the continuous phase of the emulsion.

21

22   15 Drilling fluid according to any one of the  
23       preceding Claims, containing also an oil-soluble  
24       ester in the continuous phase of the emulsion.

25

26   16 Drilling fluid substantially as hereinbefore  
27       described with reference to any one of Examples 1  
28       to 5.

29

30

31

32

33

34

35

Patents Act 1977

Examiner's report to the Comptroller under  
Section 17 (The Search Report)

Application number

GB 9215569.6

Relevant Technical fields

(i) UK CI (Edition K ) E1F (FGP)

Search Examiner

(ii) Int CI (Edition 5 ) C09K

D B PEPPER

Databases (see over)

(i) UK Patent Office

Date of Search

(ii) ONLINE DATABASE: WPI

25 AUGUST 1992

Documents considered relevant following a search in respect of claims

1-16

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
	NONE	

SF2(p)

HD - doc99\fil000196

Category	Identity of document and relevant passages	Relevance to claim(s)

#### Categories of documents

**X:** Document indicating lack of novelty or of inventive step.

**Y:** Document indicating lack of inventive step if combined with one or more other documents of the same category.

**A:** Document indicating technological background and/or state of the art.

**P:** Document published on or after the declared priority date but before the filing date of the present application.

**E:** Patent document published on or after, but with priority date earlier than, the filing date of the present application.

**&:** Member of the same patent family, corresponding document.

**Databases:** The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).